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Waste Treatability Tests of Spent Solvent and Other Organic Wastewaters

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Waste Treatability Tests of Spent Solvent and Other Organic Wastewaters

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Some commercial and industrial facilities treat RCRA spent solvent wastewaters by steam stripping, carbon adsorption, and/or biological processes. Thirteen facilities were visited by EPA's Office of Research and Development (ORD) from June 1985 to September 1986, to conduct sampling and analysis episodes and to determine the levels of performance achievable by these and other treatment processes. This paper summarizes the results of five of the tests: two steam strippers, two carbon adsorption systems, and one activated sludge biological system.

INTRODUCTION

Large volumes of organic chemical wastes are generated annually in the United States from manufacturing and processing operations. It was estimated that over 3 billion gallons of spent solvents and 24 million gallons of non-solvent halogenated wastes were generated in 1981 [*1*]. The solvent wastes were among the first hazardous waste categories to be addressed in the Hazardous and Solid Waste Amendments (HSWA) of 1984. As a result of HSWA, the Environmental Protection Agency (EPA) has studied treatment technologies that can destroy or remove toxic constituents from hazardous wastes, or immobilize them prior to land disposal.

EPA collected data from available sources on the treatability of wastes containing the F001–F005 spent solvent constituents (see Table 1) [*2*]. Sources of treatment performance data included the organic chemicals, plastics, and synthetics fibers industries data base, the pharmaceuticals industry data base, the iron and steel manufacturing point source category data base, and numerous literature resources. To supplement the historical treatment data, EPA conducted sampling episodes for organic wastes containing the constituents of F001–F005, and transferred other data based on similarity of chemical structures.

Some of the spent solvent treatability tests involved sampling waste treatment processes at commercial treatment, storage, and disposal facilities (TSDFs) and chemical production facilities. Preference was given to sampling from on-site treatment facilities where the waste of interest is treated alone or as a major component of the total waste handled. If such on-site facilities could not be identified, the second choice was commercial facilities where mixing of many wastes is generally practiced but where extensive optimization of treatment may have occurred. Where no suitable TSDF facilities are identified, in-house tests would be conducted. Eight types of waste treatment processes were sampled at thirteen commercial-scale facilities under this program. The raw wastes, treated effluents and residues were analyzed for volatile and non-volatile organics and other constituents. The eight processes included were:

- Distillation
- Agitated Thin Film Evaporation
- Screw Auger Evaporation
- Incineration
- Waste Blending/Fuel Substitution
- Steam Stripping
- Activated Sludge
- Carbon Adsorption

The data from the facilities tested are summarized in a report, which can be obtained through the National Technical Information Service [*2*].

The subsequent discussions concern the treatment technologies for spent solvent wastewaters (streams containing less than one percent total organic carbon) and the results of sampling conducted at five of the thirteen facilities. These technologies are steam stripping (two sites), activated sludge (one site), and carbon adsorption (two sites).

STEAM STRIPPING

Steam stripping is a continuous fractional distillation process in which live steam is injected directly into the bottom of a packed or tray tower to strip volatile organic compounds from aqueous wastes in multiple equilibrium stages. Steam stripping is most effective in treating

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TABLE 1. SPENT SOLVENT WASTES

Industry and EPA hazardous waste No.	Waste Description
Generic:	
F001	The following spent halogenated solvents used in degreasing: trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons; all spent solvent mixtures/blends used in degreasing containing, before use, a total of 10% or more (by volume) of one or more of the above halogenated solvents or those solvents listed in F002, F004, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F002	The following spend halogenated solvents: Tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, orthodichlorobenzene, trichlorofluoromethane, and 1,1,2-trichloroethane; all spent solvent mixtures/blends containing, before use, a total of ten percent or more (by volume) of one or more of the above halogenated solvents or those listed in F001, F004, or F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F003	The following spend non-halogenated solvents: Xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol; all spent solvent mixtures/blends containing, before use, only the above spent non-halogenated solvents; and all spent solvent mixtures/blends containing, before use, one or more of the above non-halogenated solvents, and, a total of 10% or more (by volume) of one or more of those solvents listed in F001, F002, F004, and F005; and still bottoms from the recovery of these spend solvents and spent solvent mixtures.
F004	The following spent non-halogenated solvents: Cresols and cresylic acid, and nitrobenzene; all spent solvent mixtures/blends containing, before use, a total of 10% or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, and F005; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.
F005	The following spent non-halogenated solvents: Toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine, benzene, 2-ethoxyethanol, and 2-nitropropane; all spent solvent mixtures/blends containing, before use, a total of 10% or more (by volume) of one or more of the above non-halogenated solvents or those solvents listed in F001, F002, or F004; and still bottoms from the recovery of these spent solvents and spent solvent mixtures.

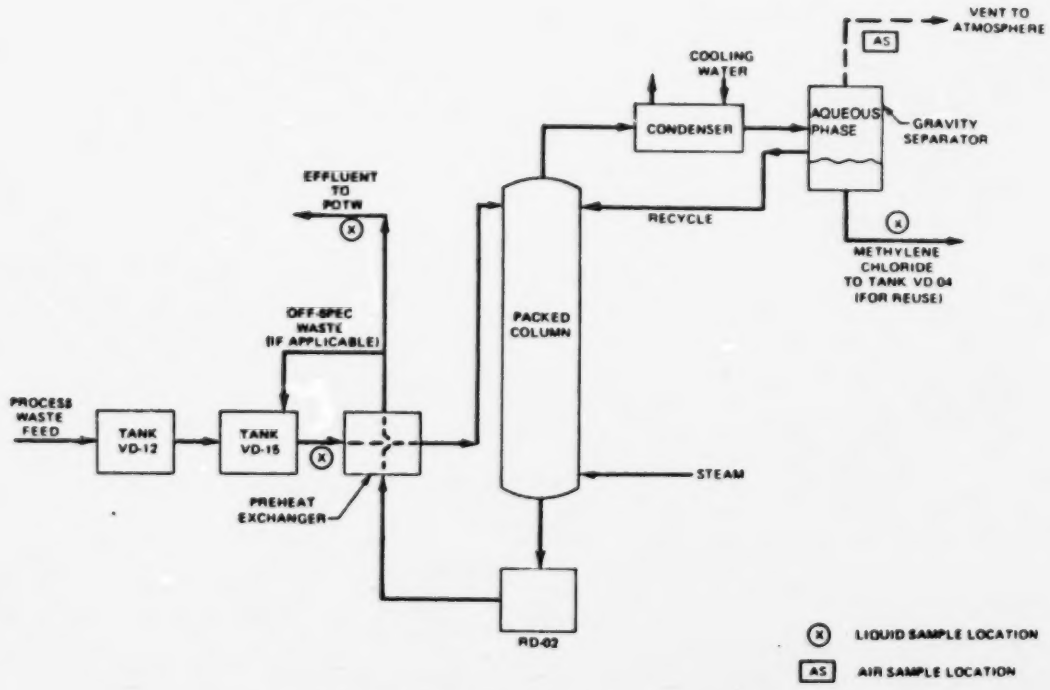

Figure 1. Facility G—methylene chloride steam stripping schematic.

TABLE 2. FACILITY G—STEAM STRIPPER ANALYTICAL DATA

Compound	Process Waste Influent		Bottoms Effluent		Overhead Condensate Organic Phase				
	Flow Rate (kg/hr)[a]	Concentration (mg/kg)	Flow Rate (kg/hr)[b]	Concentration (mg/kg)	Flow Rate (kg/hr)	Concentration (mg/kg)	Removal[d] (wt. %)	Flow Rate (kg/hr)	Concentration (mg/kg)
Methylene Chloride	4.5	3,600	$<2.6 \times 10^{-4}$	<0.19	0.088	5,110	>99.99[e]	0.095	24.7
Chloroform	0.066	52	0.0072	5.3	0.019	1,080	89	0.046	12.0
Carbon Tetrachloride	2.9×10^{-3}	<2.3	$<2.26 \times 10^{-4}$	<0.17	—	—	>92[c]	$<2.3 \times 10^{-4}$	0.06
Total Volatile Organics	4.6	3,654	7.69×10^{-3}	<5.66	0.107	6,200	>99.8	0.141	36.8
Water	1,255[f]	—	1,360[f]	—	16.9[f]	—	—	4.14	—
Total	1,260	—	1,360	—	17.0	—	—	4.28	—
Additional Parameters									
Volumetric Flows (l/min)	19.7		21.8		0.285			64.3	
Specific Gravity	1.069		1.0425		1.0167			—	

[a] Calculation: Concentration (mg/l) × Overall Flow Rate (l/hr) × 10^{-6} = kg/hr.
[b] Calculated from material and energy balances using measured flow.
[c] Outlet component concentration is below detection limit, therefore, the percent removal is calculated using the detection limit as the measured concentration.
[d] Calculated as: [1-(Effluent from Stripper)/(influent to Stripper)] × 100%.
[e] Balance of total flow after accounting for organics.

aqueous wastes containing organic compounds with low boiling points, which are relatively immiscible in water. Miscible organics such as ketones or alcohols are not as readily steam stripped. Waste streams with high concentrations of suspended solids, dissolved metals, oil, and grease may require pretreatment steps before steam stripping.

Two facilities using steam stripping to treat constituents of F001–F005 were tested. Facility G is a chemical manufacturing plant that produces a number of intermediate products used by the chemical, cosmetics, and agricultural industries. The spent solvent is methylene chloride. Facility N produces mono-carbon chlorinated solvents such as methylene chloride, chloroform and carbon tetrachloride. Their steam strippers treat an aqueous waste stream consisting of equipment washwater and rainfall collected from diked areas around the plant.

At Facility G, the process waste feed (5 gallons per minute average) to the steam stripper consisted of about 0.4% methylene chloride in water. Figure 1 illustrates their steam stripping process. The packed column has approximately five theoretical stages and was operated at approximately 101°C. Table 2 summarizes the data obtained from sampling at Facility G. The overall reduction of methylene chloride in the feed was over 99.99%. The process was less effective for chloroform (89%) and car-

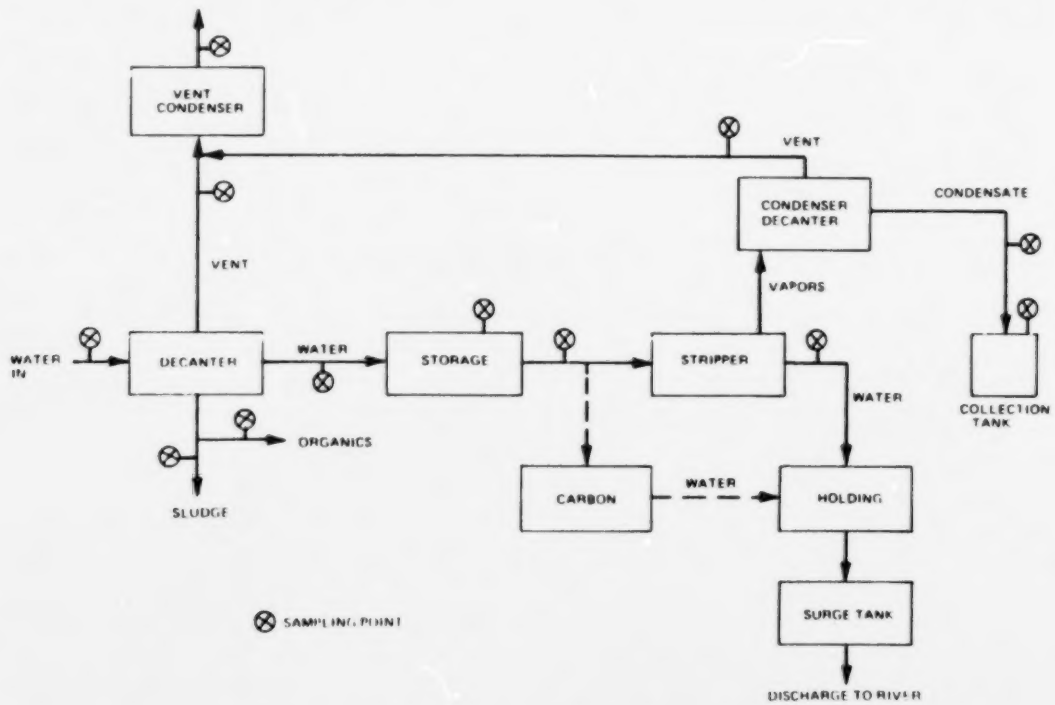

Figure 2. Facility N—steam stripping schematic and sampling points.

TABLE 3. FACILITY N—STEAM STRIPPING ANALYTICAL DATA

Compound	Stripper Influent Flow (kg/hr)[a]	Stripper Influent Conc. (mg/kg)	Stripper Effluent Flow (kg/hr)	Stripper Effluent Conc. (mg/kg)	Organic Condensate[b] Flow (kg/hr)	Organic Condensate[b] Conc. (mg/l)	Percent Removal (wt. %)	Primary Condenser Vent Flow (kg/hr)
Chloromethane	0.0796	33	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.98[c]	0.0086
Methylene Chloride	10.96	4,490	$<2.88 \times 10^{-5}$	<0.011	9.42	1,180,000	>99.999[c]	1.05
Chloroform	3.19	1,270	$<1.67 \times 10^{-5}$	<0.006	2.78	319,000	>99.999[c]	0.160
Carbon Tetrachloride	0.316	55	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.99[c]	0.014
Trichloroethylene	.028	5.6	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.9[c]	—
1,1,2-Trichloroethane	.013	5.3	$<1.35 \times 10^{-5}$	<0.005	—	—	>99.9[c]	—
Total Volatile Organics	14.6	5,860	$<9.95 \times 10^{-5}$	<0.037	12.2	1,499,000	>99.999[c]	1.23
Water	2,425	—	2,680	—	—	—	—	0.013
Additional Parameters								
Flow Rates (l/min)	40.7	—	44.7	—	0.14	—	—	57
Specific Gravity	1.0	—	1.0	—	—	—	—	—

[a] Calculation [Concentration (mg/l) ÷ (1.069 kg/l)] × Flow Rate (l/hr) (10^{-6}) = kg/hr.
[b] Condensate rate estimated from organics in with feed minus organics out with uncondensed vapor and bottoms.
[c] Outlet component concentration is below detection limit, therefore, the percent removed is calculated using the detection limit as the measured concentration.
[d] Calculated as: (1-(Effluent from Stripper)/(influent to Stripper)) × 100%.

bon tetrachloride (92%). The bottoms from the steam stripper are discharged to the local sanitary sewer.

Figure 2 illustrates the steam stripping process at Facility N and Table 3 summarizes the data obtained. The influent flow was about 11 gallons per minute (41 liters per minute). On an average basis, methylene chloride, chloroform and carbon tetrachloride removals were all over 99.98%. The stripper bottoms are discharged to a nearby river under current NPDES permit restrictions.

The two steam stripping systems were effective at reducing the volatile organic components in the waste streams, and in recovery of spent solvents.

ACTIVATED SLUDGE

Typical activated sludge treatment processes metabolize many dissolved compounds by biologically catalyzed oxidation to carbon dioxide, water, and biomass. The process generally begins with primary treatment (equalization, screening, sedimentation), then the influent wastewater is pumped to a basin or tank where aerobic microorganisms are suspended. Effluent from the basin goes to a clarifier for settling of biological sludge. A portion of this sludge is returned to the aeration basin to maintain an optimum biomass concentration in the sys-

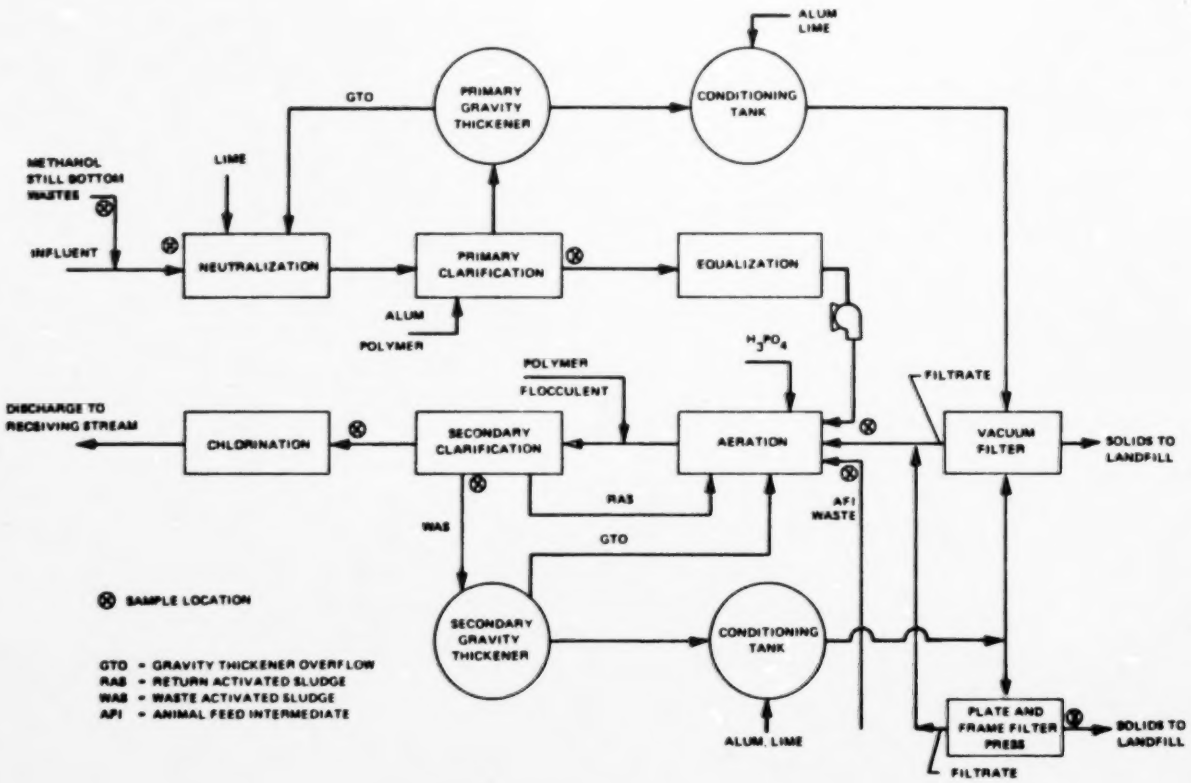

Figure 3. Biological wastewater treatment plant facility 1.

TABLE 4. FACILITY I—ACTIVATED SLUDGE ANALYTICAL DATA

Pollutant	Units	Calc. Average Meth. Still Bottoms	Calc. Average Influent to Aeration	Calc. Average AFI+ Influent	Calc. Average Secondary Effluent	Calc. Average Waste Act. Sludge
VOLATILE ORGANIC COMPOUNDS						
methylene chloride	µg/l	7.3	84	40	33	537*
acetone (2-propanone)	µg/l	19	774	<113	49	84*
2-butanone (MEK)	µg/l	<10	131	<35	47	22*
4-methyl-2-pentanone	µg/l	<10	2,557	<34	47	15*
toluene	µg/l	<5	1,459	<18	24	<5*
chlorobenzene	µg/l	<5	540	<18	24	<5*
methanol	µg/l	697,778	56,667	<10,000	<10,000	<10,000*
SEMI-VOLATILE ORGANIC COMPOUNDS						
2-chlorophenol	µg/l	75	22	<22	22	55*
METALS						
zinc	mg/kg	5.1	39	<13	17	1033*
OTHER ANALYSES						
BOD5	mg/l BOD	525	120	1,396	9.8	
TOC	mg/l	4198	99	1040	13	
oil & grease	mg/l	2174	28	443	55	
pH	pH units	4.4	5.9	8.3	6.4	6.5

* = Units are µg/kg.
+ AFI = Animal Feed Intermediate.
Analyte concentrations below detection limits were considered at the detection limit for calculations of averages.

tem. Nutrients may be added to the basin for optimum biological activity. Mixing and aeration are provided for the oxidation reactions.

Facility I manufactures plastic adhesives, ultraviolet light absorbers, surfactants, and animal feed intermediate (AFI). The waste stream of interest is the bottom waters from a continuous methanol recovery stripper. This stream is mixed with wastewaters from the other processes and treated by a 3.5 million gallon per day capacity three-day hydraulic residence activated sludge plant (Figure 3). The methanol waste stream constituted about 0.1% of the influent flow and contained about 0.05% methanol. Table 4 summarizes the analytical data obtained from the testing. Methanol concentrations in nine still bottom grab samples collected during the three-day sampling program ranged from 350 to 1,600 mg/l. The average concentration was about 700 mg/l. Apparent methanol removals by the biological treatment system

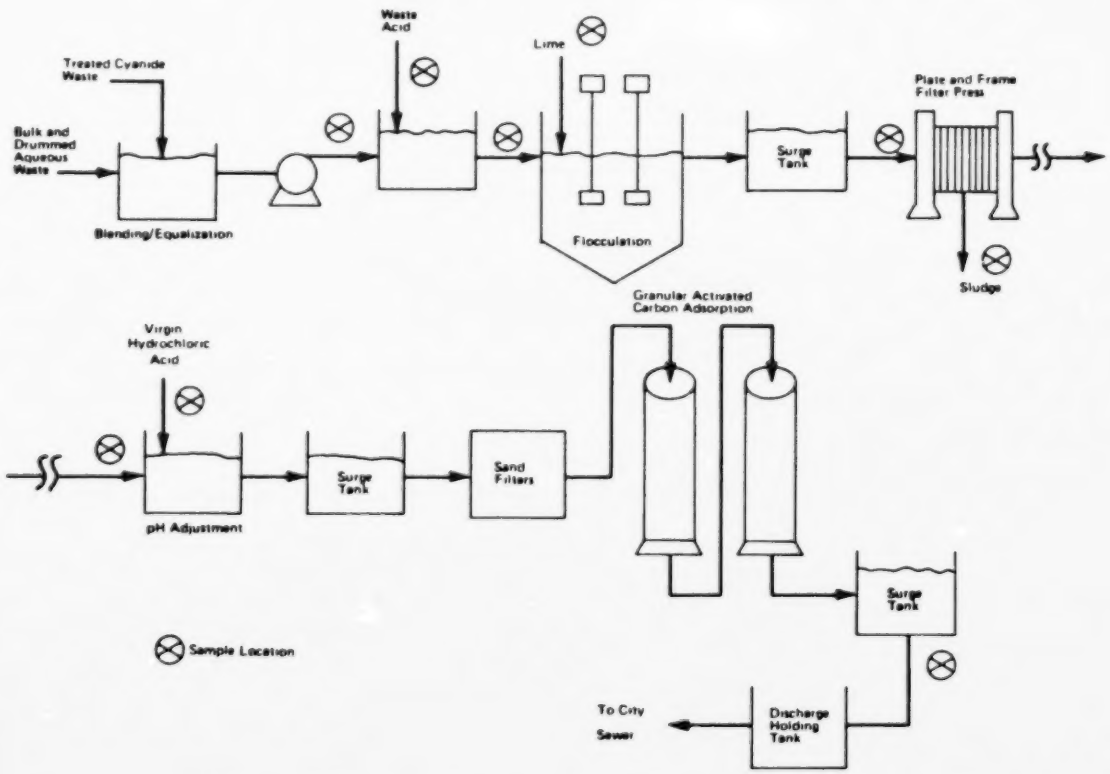

Figure 4. Facility B flow diagram/sample points for aqueous waste treatment system.

TABLE 5. FACILITY B—CARBON ADSORPTION DATA

Parameter	Units	Day 1 Filtrate	Day 1 GAC Effluent	Day 2 Filtrate	Day 2 GAC Effluent	Day 3 Filtrate	Day 3 GAC Effluent
VOC							
Methylene chloride	µg/L	220,000	<1,250	43,000	<2,500	130,000	30,000
Acetone	µg/L	68,000	140,000	61,000	160,000	69,000	55,000
2-butanone (MEK)	µg/L	<5,000	<2,500	6,600	<5,000	7,000	<5,000
1,1,1-trichloroethane	µg/L	ND	ND	2,500	<1,000	1,600	1,600
Trichloroethene	µg/L	4,200	<500	1,400	<1,000	<1,000	<1,000
Toluene	µg/L	13,000	<500	7,700	<1,000	3,900	<1,000
Total xylenes	µg/L	<1,000	<500	8,000	<1,000	<1,000	<1,000
Acid Extractables							
P-chloro-m-cresol	µg/L	5,600	<100	1,600	<100	<500	<100
2-nitrophenol	µg/L	1,200	<100	1,600	<100	3,000	<100
4-nitrophenol	µg/L	1,100	<100	2,300	<100	1,400	<100
2,4-dinitrophenol	µg/L	120	<100	<400	<100	ND	ND
Phenol	µg/L	19,000	<100	4,200	<100	5,100	<100
Base/Neutral Extractables							
N-nitrosodimethylamine	µg/L	100	<100	ND	ND	ND	ND
Metals							
Cadmium	mg/L	1.2	0.15	7.9	0.51	50	1.4
Hex. chromium	mg/L	NS	<20	NS	<5	NS	<5
Total chromium	mg/L	2.1	0.091	1.9	0.12	0.068	0.091
Copper	mg/L	160	0.32	170	0.87	380	0.56
Lead	mg/L	1.4	0.56	0.82	0.74	0.67	0.63
Nickel	mg/L	2.2	2.2	2.3	2.0	22	1.8
Zinc	mg/L	24	1.4	16	1.6	46	0.70

ND = Not determined
NS = Not Sampled

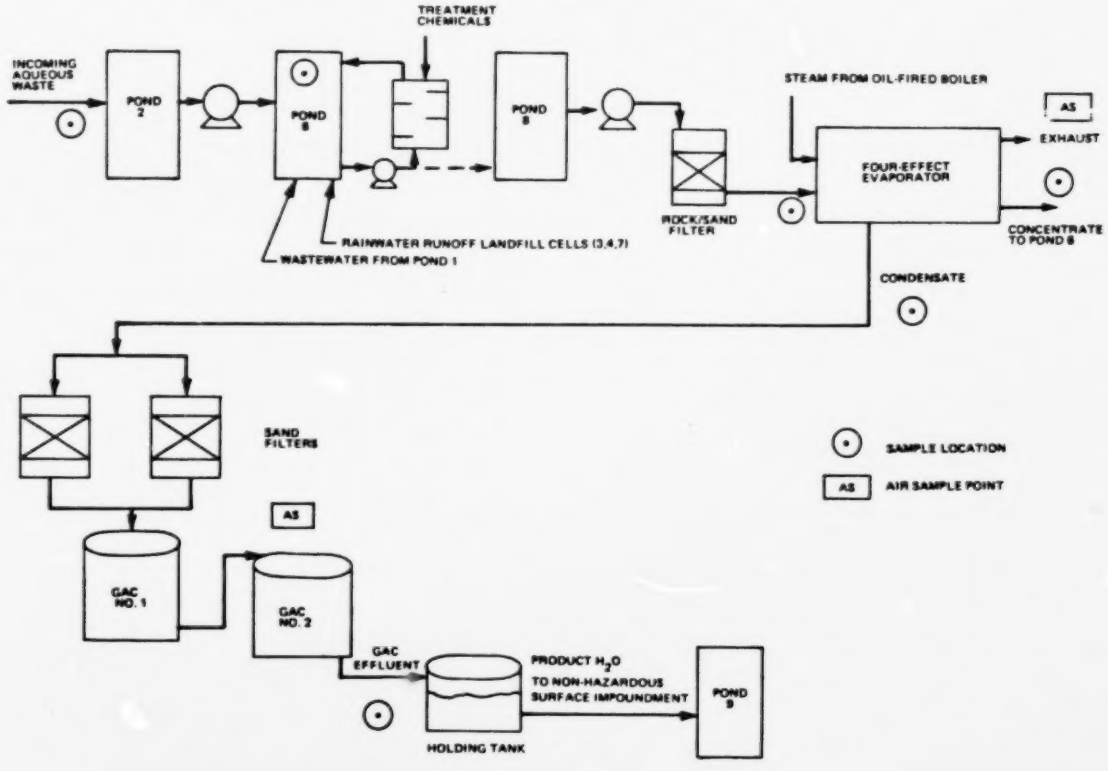

Figure 5. Flow diagram/sample points for aqueous waste treatment at facility C.

TABLE 6. FACILITY C—CARBON ADSORPTION DATA

Parameter	Units	Day 1		Day 2		Day 3	
		Evaporator Condensate	GAC Effluent	Evaporator Condensate	GAC Effluent	Evaporator Condensate	GAC Effluent
VOC							
Methylene chloride	µg/L	34	<5	<5	<5	15	<5
Acetone	µg/L	710	<50	800	<50	850	<50
2-Butanone (MEK)	µg/L	<50	<10	360	<10	230	<10
1,1,1-trichloroethane	µg/L	<10	<2	<10	<10	34	<2
Trichloroethene	µg/L	<10	<2	<2	<2	7.5	<2
Benzene	µg/L	<10	<2	ND	ND	21	<2
4-methyl-2-pentanone	µg/L	<50	<10	26	<10	31	<10
Tetrachloroethene	µg/L	<10	<2	<2	<2	6.5	<2
Toluene	µg/L	<10	<2	9	<2	62	<2
Ethyl benzene	µg/L	<10	<2	<2	<2	5.5	<2
Total xylenes	µg/L	<10	<2	<2	<2	26	<2
Acid Extractables							
2,4-dichlorophenol	µg/L	ND	ND	37	<20	ND	ND
2-nitrophenol	µg/L	222	<20	75	<20	ND	ND
Base/Neutral Extractables							
Bis (2-chloroethyl) ether	µg/L	86	<20	<20	<20	ND	ND
Diethyl phthalate	µg/L	547	<20	<20	<20	<10	<10
isophorone	µg/L	ND	ND	21	<20	26	<10
Metals							
Zinc	mg/L	.0053	.027	<.005	<.005	.016	.013

ND = Not Determined

ranged from over 64% to over 94%. The analytical method detection limit of 10 mg/l precluded a more accurate determination of removal efficiency. Total organic carbon (TOC) and biochemical oxidation demand (BOD) removals were 85 and 94% respectively.

CARBON ADSORPTION

Activated carbon is used for removal of dissolved organic compounds from aqueous wastes. Organic molecules are attracted to the surface and pores of the activated carbon by physical and/or chemical forces. The effectiveness of activated carbon for adsorption is related to its large surface area. Surface area of typical activated carbons can range from 500 to 1,400 square meters per gram of material. In a typical fixed-bed adsorption system, wastewater flows through a vessel or bed filled with granular activated carbon, at rates from 2 to 5 gallons per minute per square foot. Flow continues until a specific volume has been treated or until one of the wastewater constituents exceeds a predetermined concentration in the bed effluent (breakthrough). At this point, the bed is taken out of service and the carbon is either discarded or regenerated offsite in a special furnace. Adsorption is most effective when the organic compounds to be removed have relatively high molecular weights, high boiling points, low aqueous solubilities, and low polarity.

Carbon adsorption was the final treatment operation in the aqueous waste treatment processes at two commercial TSDFs, Facility B and C. In both cases, granular activated carbon was used to remove dissolved organics after upstream operations removed metals and suspended solids.

Unit processes for treatment of aqueous wastes at Facility B include pH adjustment, chemical reduction, precipitation of metals, filtration, and carbon adsorption. The principal organic compounds measured in the influent were methylene chloride, acetone, toluene, nitropropane, and phenol. The waste treatment system is shown in Figure 4.

Phenol is used as an indicator for carbon breakthrough by Plant B. This is noted by a significant increase in the effluent concentration, generally about 5 to 10% of the influent concentration. Facility B's sewer discharge permit limitation for phenol is 6.16 mg/l. The phenol breakthrough normally occurs after about 20 to 25 days of operation, according to plant personnel. Table 5 summarizes analytical data for Facility B's carbon adsorption process. The total organic carbon removal averaged 90%. The phenol removal was 97%. The lower molecular weight organics (methylene chloride, acetone) were removed to a lesser degree.

Facility C's treatment of aqueous wastes included pH adjustment, precipitation of metals, filtration, and multiple-effect evaporation. Figure 5 is the flow diagram of the entire waste treatment process. The carbon adsorption system was used to further reduce the organic content of the wastewater. As shown in Table 6, the primary organic compounds in the adsorber influent were acetone and methyl ethyl ketone. The total organic carbon was reduced by 98% in C's adsorption operation.

CONCLUSION

In general, all three treatment techniques effectively removed specific volatile organic compounds to low residual concentrations. The summaries presented in this paper and the cited references may be of interest to those seeking data on the treatability of similar organic wastewaters. Each of the five case studies are discussed in greater detail elsewhere [2].

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1. US EPA, National Survey of Hazardous Waste Generators and TSDFs Regulated under RCRA in 1981, Office of Solid Waste, April 1984.
2. Field Measurements of Full-Scale Hazardous Waste Treatment Facilities—Organic Solvent Wastes, EPA report, October 1988. NTIS No. (PB89-138853)

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